

CHROM. 18 072

## Note

### Liquefied gases as eluents for thin-layer chromatography

GIORGIO NOTA\*, CARLO IMPROTA and ANTONIO CANNATA

*Dipartimento di Chimica, Università di Napoli, via Mezzocannone, 4, 80134 Naples (Italy)*

(Received July 30th, 1985)

A few studies have been published<sup>1–3</sup> in which liquefied gases were used as eluents for high-performance liquid chromatography (HPLC). These eluents generally have lower viscosity than the common organic solvents, which makes the chromatographic process more efficient and consequently a lower pressure is needed to transport the liquefied gas through the column. Additionally, the physical peculiarities of subcritical fluids, particularly CO<sub>2</sub> and N<sub>2</sub>O, favour the use of the most convenient detection systems, such as the mass spectrometer and the flame ionization

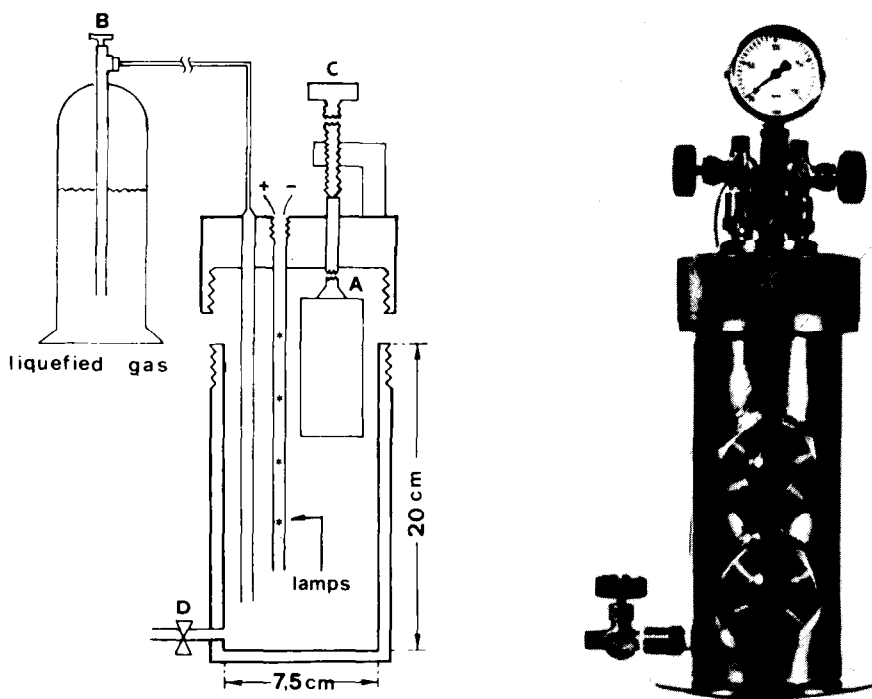


Fig. 1. Schematic diagram and photograph of the chromatographic apparatus employed for TLC using liquefied gases as eluents.

TABLE I  
SPECIFICATIONS OF THE AUTOCLAVE EMPLOYED

|                         |  |
|-------------------------|--|
| Internal height         | 20 cm  |
| Internal diameter       | 7.5 cm   |
| Volume                  | 0.95 l   |
| Maximum pressure of use | 75 bar   |
| Construction materials  | AISI 304, bronze, PTFE, Plexiglass GS 233, GACO rubber |

detector, widely adopted in gas chromatography. As the chromatographic process and the problems typical of HPLC are generally similar to those encountered in thin-layer chromatography (TLC), we decided to investigate the possibility of using liquid CO<sub>2</sub> as an eluent in TLC<sup>4</sup>. The interesting results obtained prompted us to extend the investigation to other fluids under subcritical conditions, such as N<sub>2</sub>O, Freon 22, propene, propane and *n*-butane.

#### EXPERIMENTAL

##### Reagents

The compounds tested were pure products from Fluka (Buchs, Switzerland). Fluorescent silica gel (60 F<sub>254</sub>), silica gel 40 and reversed-phase (Stratocrom SI F<sub>254</sub>)

TABLE II

R<sub>F</sub> VALUES OBTAINED FOR DIFFERENT COMPOUNDS ON A SILICA THIN LAYER USING LIQUEFIED GASES AND *n*-HEXANE AS ELUENTS

| Compound                | N <sub>2</sub> O | Freon 22 | Propene | Propane | <i>n</i> -Butane | <i>n</i> -Hexane |
|-------------------------|------------------|----------|---------|---------|------------------|------------------|
| <i>n</i> -Pentadecane   | 1.00             | 0.70     | 0.78    | 0.80    | 0.77             | 0.57             |
| <i>n</i> -Octadecane    | 1.00             | 0.70     | 0.78    | 0.80    | 0.77             | 0.57             |
| 1-Decanol               | 0.06             | 0.13     | 0.06    | 0.02    | 0.03             | 0.05             |
| 1-Hendecanol            | 0.06             | 0.13     | 0.06    | 0.02    | 0.03             | 0.05             |
| 1-Dodecanol             | 0.06             | 0.13     | 0.06    | 0.02    | 0.03             | 0.05             |
| Lauric acid             | 0.18             | 0.15     | 0.16    | 0.03    | 0.03             | 0.00             |
| Myristic acid           | 0.10             | 0.05     | 0.13    | 0.03    | 0.03             | 0.00             |
| Palmitic acid           | 0.00             | 0.00     | 0.05    | 0.03    | 0.03             | 0.00             |
| Methyl laurate          | 0.15             | 0.47     | 0.30    | 0.05    | 0.15             | 0.13             |
| Methyl myristate        | 0.15             | 0.44     | 0.30    | 0.05    | 0.15             | 0.13             |
| Methyl palmitate        | 0.15             | 0.41     | 0.30    | 0.05    | 0.15             | 0.13             |
| <i>o</i> -Cresol        | 0.17             | 0.30     | 0.16    | 0.00    | 0.09             | 0.00             |
| <i>m</i> -Cresol        | 0.17             | 0.26     | 0.14    | 0.00    | 0.09             | 0.00             |
| <i>p</i> -Cresol        | 0.17             | 0.28     | 0.14    | 0.00    | 0.09             | 0.00             |
| <i>o</i> -Xylene        | 0.00             | 0.10     | 0.00    | 0.00    | 0.00             | 0.00             |
| <i>m</i> -Xylene        | 0.00             | 0.10     | 0.00    | 0.00    | 0.00             | 0.00             |
| <i>p</i> -Xylene        | 0.00             | 0.10     | 0.00    | 0.00    | 0.00             | 0.00             |
| Fluorene                | 0.29             | 0.49     | 0.32    | 0.14    | 0.18             | 0.28             |
| Anthracene              | 0.56             | 0.50     | 0.32    | 0.12    | 0.17             | 0.23             |
| Phenanthrene            | 0.33             | 0.52     | 0.32    | 0.15    | 0.22             | 0.28             |
| Fluoranthene            | 0.55             | 0.51     | 0.33    | 0.12    | 0.15             | 0.23             |
| Pyrene                  | 0.45             | 0.51     | 0.32    | 0.12    | 0.22             | 0.25             |
| Methylpyrene            | 0.53             | 0.49     | 0.34    | 0.12    | 0.22             | 0.               |
| Benzo[ <i>a</i> ]pyrene | 0.28             | 0.47     | 0.24    | 0.07    | 0.13             | 0.16             |

C<sub>18</sub>W) thin layers were obtained from Carlo Erba (Milan, Italy). Reversed-phase (C<sub>18</sub>) HPTLC thin layers were obtained from Merck (Darmstadt, F.R.G.). Liquid N<sub>2</sub>O, Freon 22 (CHClF<sub>2</sub>), propene, propane and *n*-butane cylinders equipped with an eductor tube were purchased from SON (Naples, Italy).

#### Chromatographic apparatus

A special autoclave (Fig. 1), devised and constructed in collaboration with SON, was used as the chromatographic apparatus. The main characteristics of the autoclave are reported in Table I. The layer bearing the sample is attached to the moveable support A. The lock is applied on the bomb and solvent under subcritical conditions is introduced from a reservoir equipped with an eductor tube, by keeping valve B open. When a sufficient amount of liquid has been introduced, valve B is closed and the lower edge of the layer is introduced into the liquid phase by acting on the support C. When the solvent has reached the upper edge of the layer, it is allowed to evaporate by opening valve D; then the lock is removed and the layer is recovered. Spots are detected by means of iodine or UV light. All the stages of the experiment may be conveniently checked by observing, through two quartz windows, the inside of the adequately illuminated autoclave.

TABLE III

*R<sub>F</sub>* VALUES OBTAINED FOR DIFFERENT COMPOUNDS ON REVERSED-PHASE (C<sub>18</sub>) THIN LAYERS USING LIQUEFIED GASES AND *n*-HEXANE AS ELUENTS

| Compound                | N <sub>2</sub> O | Freon 22 | Propene | Propane | <i>n</i> -Butane | <i>n</i> -Hexane |
|-------------------------|------------------|----------|---------|---------|------------------|------------------|
| <i>n</i> -Pentadecane   | 0.69             | 0.73     | 0.80    | 0.85    | 0.81             | 0.62             |
| <i>n</i> -Octadecane    | 0.49             | 0.67     |         |         |                  |                  |
| 1-Decanol               | 0.35             | 0.47     | 0.24    | 0.18    | 0.17             | 0.32             |
| 1-Hendecanol            | 0.21             | 0.40     | 0.18    | 0.16    | 0.13             | 0.25             |
| 1-Dodecanol             | 0.10             | 0.29     | 0.14    | 0.12    | 0.06             | 0.14             |
| Lauric acid             | 0.36             | 0.42     | 0.54    | 0.15    | 0.24             | 0.27             |
| Myristic acid           | 0.27             | 0.19     | 0.43    | 0.14    | 0.21             | 0.23             |
| Palmitic acid           | 0.09             | 0.08     | 0.28    | 0.13    | 0.16             | 0.19             |
| Methyl laurate          | 0.68             |          | 0.73    | 0.22    | 0.46             | 0.50             |
| Methyl myristate        | 0.60             |          | 0.70    | 0.20    | 0.44             | 0.46             |
| Methyl palmitate        | 0.55             | 0.65     | 0.68    | 0.18    | 0.42             | 0.42             |
| <i>o</i> -Cresol        | 0.56             | 0.59     | 0.41    | 0.00    | 0.24             | 0.29             |
| <i>m</i> -Cresol        | 0.50             | 0.64     | 0.36    | 0.00    | 0.27             | 0.33             |
| <i>p</i> -Cresol        | 0.42             | 0.58     | 0.41    | 0.00    | 0.12             | 0.30             |
| <i>o</i> -Xylene        | 0.29             | 0.34     | 0.20    | 0.08    | 0.00             | 0.29             |
| <i>m</i> -Xylene        | 0.20             | 0.35     | 0.21    | 0.09    | 0.00             |                  |
| <i>p</i> -Xylene        | 0.37             | 0.39     | 0.24    | 0.12    | 0.00             | 0.21             |
| Fluorene                | 0.33             | 0.59     | 0.53    | 0.30    | 0.35             | 0.49             |
| Anthracene              | 0.31             | 0.57     | 0.53    | 0.32    | 0.34             | 0.49             |
| Phenanthrene            | 0.43             | 0.59     | 0.62    | 0.34    | 0.43             | 0.52             |
| Fluoranthene            | 0.33             | 0.56     | 0.53    | 0.28    | 0.35             | 0.47             |
| Pyrene                  | 0.24             | 0.52     | 0.47    | 0.34    | 0.35             | 0.50             |
| Methylpyrene            | 0.24             | 0.52     | 0.47    | 0.32    | 0.35             | 0.50             |
| Benzo[ <i>a</i> ]pyrene | 0.12             | 0.39     | 0.31    | 0.18    | 0.22             | 0.43             |

TABLE IV

AVERAGE VELOCITIES OBSERVED ON THIN LAYERS OF VARIOUS TYPES OF 10 cm LENGTH

| Eluent           | Average velocity (cm/min) |                      |                                 |                 |                            |
|------------------|---------------------------|----------------------|---------------------------------|-----------------|----------------------------|
|                  | SiO <sub>2</sub> -60      | SiO <sub>2</sub> -40 | SiO <sub>2</sub> -60<br>(HPTLC) | C <sub>18</sub> | C <sub>18</sub><br>(HPTLC) |
| Propane          | 0.59                      | 1.15                 | 0.53                            | 1.56            | 0.70                       |
| Propene          | 0.9                       | 1.18                 | 0.6                             | 1.26            | 0.73                       |
| <i>n</i> -Butane | 0.94                      | 1.40                 | 0.76                            | 1.51            | 0.88                       |
| Freon 22         | 0.40                      | 0.60                 | —                               | 0.50            | 0.44                       |
| <i>n</i> -Hexane | 0.57                      | 0.87                 | 0.42                            | 0.95            | 0.45                       |
| Methanol         | 0.27                      | 0.40                 | 0.27                            | 0.56            | 0.30                       |

## RESULTS AND DISCUSSION

The  $R_F$  values of various compounds obtained on thin layers of silica gel or the reversed phase, using propane, *n*-butane, propene, N<sub>2</sub>O and Freon 22, are reported in Table II and III.  $R_F$  values obtained with *n*-hexane, which is a non-polar eluent, are also reported.

As expected, the eluent properties of propane and *n*-butane are similar to those of *n*-hexane, whereas propene, N<sub>2</sub>O and Freon 22 behave as polar eluents. In Table IV the average migration velocities of subcritical fluids, *n*-hexane and methanol, observed on thin layers of various types, are reported. All the subcritical fluids tested show a higher average velocity than those exhibited by *n*-hexane and methanol, because of their low viscosity. On the other hand, N<sub>2</sub>O advances only 10 cm during 40 min.

The apparatus described here is easily handled; the use of a transparent autoclave allows one to follow the chromatographic process directly and makes TLC with liquefied gases as simple as normal techniques. The easy removal of the eluent should also be emphasized with respect to the re-elution of the layer and to the use of a flame ionization detector for TLC.

## REFERENCES

- 1 T. Takeuchi, Y. Watanabe, K. Matsuoka and D. Ishii, *J. Chromatogr.*, 216 (1981) 153.
- 2 T. Takeuchi and D. Ishii, *J. Chromatogr.*, 239 (1982) 633.
- 3 H. H. Lauer, D. McManigill and R. Board, *Anal. Chem.*, 55 (1983) 1370.
- 4 G. Nota, C. Improta and A. Cannata, *J. Chromatogr.*, 285 (1984) 194.